Indian J. Phys. 73A (2), 175–182 (1999)

IJP A
— an international journal

Effect of chromium impurity on the dc resistivity of lithium antimony ferrite

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Received 28 April 1997, accepted 10 September 1998

Abstract : Polycrystalline samples of mixed ferrite system $Li_{0.6}Cr_xSb_{0.1}Fe_{2.3-x}O_4$ ($0 \leq x \leq 1.0$, where x is varied in steps of 0.2) were synthesised by the standard double sintering ceramic technique. X-ray diffraction analysis confirmed all the samples to be single phase spinels and the value of the lattice parameter was found to decrease with increasing substitution of chromium. The influence of chromium substitution on the dc resistivity of the Li–Sb ferrite samples has been discussed. The room temperature dc resistivity was found to increase with x. This has been attributed to electron hopping and cation distribution. The variation of resistivity with temperature showed a change in slope for all the samples studied. Two different regions having different activation energies were observed. This has been explained in terms of electronic and ionic conduction mechanisms. The variation of resistivity with applied field (0–50 v/cm) is also reported in this paper.

Keywords : DC resistivity, activation energy, hopping mechanism

PACS Nos. : 75.50.Gg, 72.20.–i, 61.10.–i

1. Introduction

Lithium ferrites have found wide applications at microwave frequencies because of their remarkably high electrical resistivity, low losses and excellent rectangular hysteresis loop properties. These properties can be suitably modified to get desired qualities for some specific applications by controlling the atmosphere and method of preparation. Various workers [1–4] have reported the influence of substituents like Zn^{2+}, Ti^{4+} and Cr^{3+} on the electrical properties of Li-ferrites. In this paper, we report a systematic investigation on the compositional variation of the lattice parameter, Curie temperature and dc resistivity of the

Li–Sb ferrites substituted with Cr^{3+}. The dc resistivity is also studied as a function of temperature and applied field.

2. Experimental details

The samples having the composition $Li_{0.5+z}Cr_xSb_zFe_{2.5-2z-x}O_4$ (with $z = 0.1$ and $0 \leq x \leq 1.0$, where x is varied in steps of 0.2) were synthesized by the standard double sintering ceramic technique. Analytical reagent grade Li_2CO_3, Fe_2O_3, Sb_2O_3 and Cr_2O_3 were taken in suitable proportions and thoroughly mixed in an agate jar mill in the presence of acetone to improve the homogeneity and then calcined at 850°C in air for 5 hrs. A small amount (0.5% by weight) of Bi_2O_3 was added in order to lower the sintering temperature and hence avoid volatilization of lithia which occurs at higher temperature. The whole mixture was wet milled again, dried and a small quantity of polyvinyl alcohol was added as a binder. The granulated mixture was pelleted and finally sintered in air at 1150°C for 5 hrs and then furnace cooled. Necessary grinding of the pellets was done in order to remove any oxide layer formed on the surface during sintering. The samples were characterized by X-ray diffraction (XRD) method and the single phase spinel structure of all the samples were confirmed.

Curie temperature (T_c) was measured using a simple set up given by Soohoo [5]. A small piece of the ferrite sample was magnetically attached to the lower end of a vertically placed bar magnet, which was then placed inside an electric furnace. The temperature of the furnace was gradually raised until the ferrite sample drops down. This temperature at which the ferrite loses its magnetization and drops down under gravity gives the Curie temperature (T_c) of the sample. The electrical resistivity measurements were carried out on pellets of 11 mm diameter and a uniform thickness of 2 mm, in the temperature range 298 K to 473 K. Electrical contacts were made using air dried silver epoxy on freshly ground surface of the pellets. For studying the temperature variation of resistivity, the sample was kept inside a heating cell and sufficient time was allowed for it to maintain thermal equillibrium. A chromel-alumel thermocouple was used to measure the temperature.

3. Results and discussion

The single phase spinel structure of all the samples were confirmed from the XRD patterns. Typical XRD results for the samples having $x \leq 0.6$ are shown in Figure 1. From the observed 'd' value, the corresponding lattice parameter 'a' was calculated. Its variation with chromium content is shown in Figure 2(a), and a decrease is observed with increasing Cr^{3+} substitution. The observed variation can be explained in terms of different ionic radii of the cations involved. In the present system $Li_{0.6}Cr_xSb_{0.1}Fe_{2.3-x}O_4$, Cr^{3+} ions with ionic radii 0.64 Å replaces Fe^{3+} ion with larger ionic radii 0.67 Å [6,7]. As a result, the lattice parameter is observed to decrease with increasing chromium concentration. The variation of

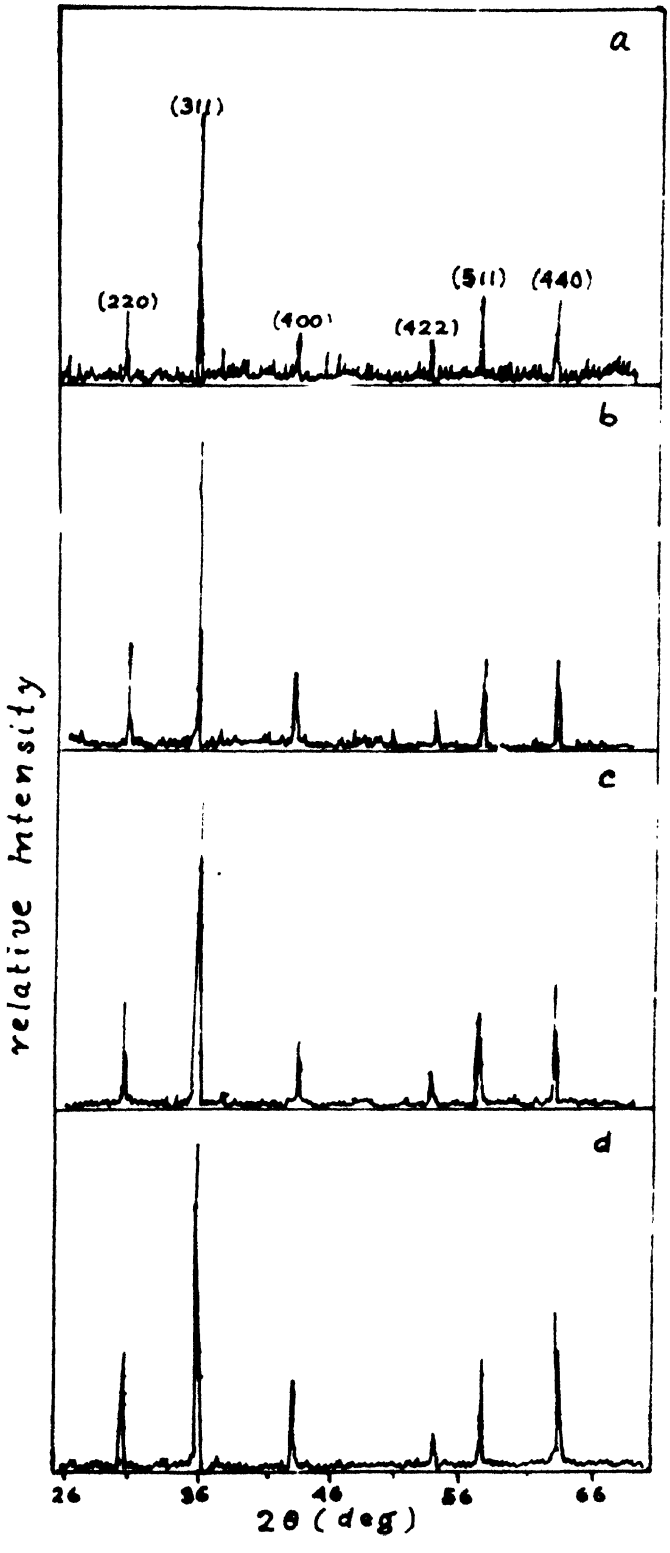

Figure 1. XRD pattern of $La_{0.6}Cr_xSb_{0.1}Fe_{2.3-x}O_4$ ferrite : (a) $x = 0.0$, (b) $x = 0.2$, (c) $x = 0.4$ and (d) $x = 0.6$

Curie temperature (T_c) with composition is shown in Figure 2(b). It is observed that the Curie temperature decreases with the increase of chromium concentration.

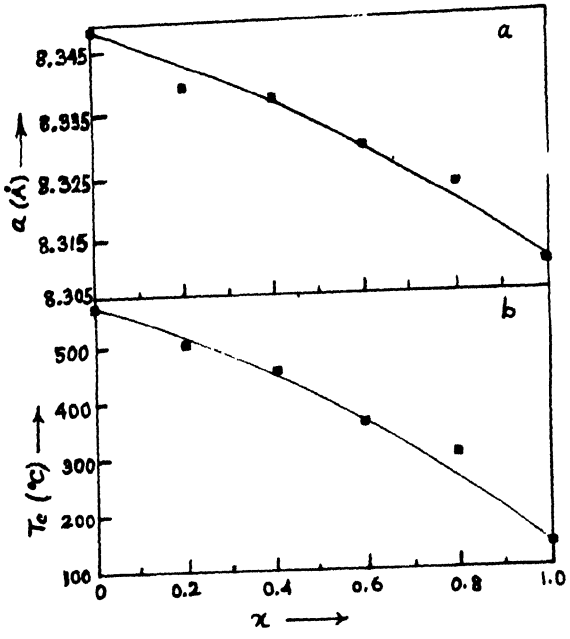

Figure 2. (a) Variation of lattice parameter with composition, (b) Curie temperature as a function of chromium concentration.

An increase in room temperature resistivity is observed with increase in the chromium content as shown in Figure 3. The conduction mechanism in ferrites is quite

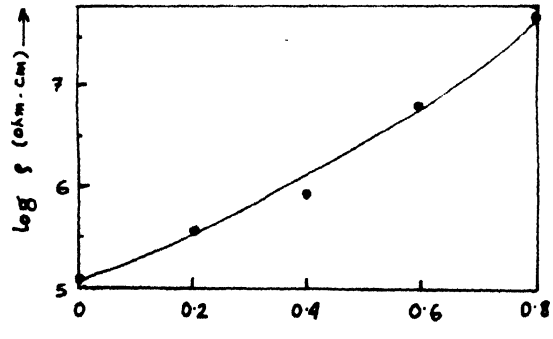

Figure 3. Compositional dependence of resistivity (log ρ) at room temperature.

different from that in semiconductors, and is not understood very clearly. Many models like electron hopping model, polaron model, phonon induced tunnelling *etc.* have been suggested to account for their electrical properties [8,9]. Unlike in semiconductors wherein the charge carriers occupy states in wide energy band, the charge carriers are localised at

the magnetic atoms. In ferrites, the cations are surrounded by close-packed oxygen anions and can well be treated as isolated from each other, as a first approximation. There will be little direct overlap of the anion charge clouds or orbitals. The electrical conduction in ferrites is therefore explained by the Verwey model of electron hopping [8]. This mechanism involves exchange of electrons between ions of the same element present in different valence state, and distributed randomly over crystallographically equivalent lattice sites. In the present series of ferrites, the conduction is taken to be due to the exchange of 3*d* electrons between Fe^{2+} and Fe^{3+} ions in the octahedral sites [10]. The appearance of Fe^{2+} ions may be due to the partial evaporation of Li^{1+} ions during the sintering process at high temperatures. In addition, there may be a slight oxygen deficiency since Fe_2O_3 is able to lose oxygen when heated at elevated temperatures, which may also give rise to some Fe^{2+} ions [11]. The Fe^{2+} ions that are formed preferentially occupy the B-site. Therefore, AA hopping does not take place. Also since AB distance is larger than the BB distance, the dominant mode of conduction is the BB hopping between Fe^{2+} and Fe^{3+} ions. The observed increase in resistivity with chromium concentration (Figure 3) can be understood on the consideration of the cation distribution along with the hopping mechanism $Fe^{2+} + Fe^{3+} \leftrightharpoons Fe^{3+} + Fe^{2+}$. The cation distribution for the composition $Li_{0.6}Cr_xSb_{0.1}Fe_{2.3-x}O_4$ is expected to be

$$(Li_{0.1}Fe_{0.9})\,[Li_{0.5}Cr_xSb_{0.1}Fe_{1.4-x}]\,O_4. \qquad (1)$$

It is known that Cr^{3+} ion has strong preference for the six-fold coordination [7]. The Li^{1+} ion tends to occupy the B-site, but above a concentration of 0.5, it start drifting to the

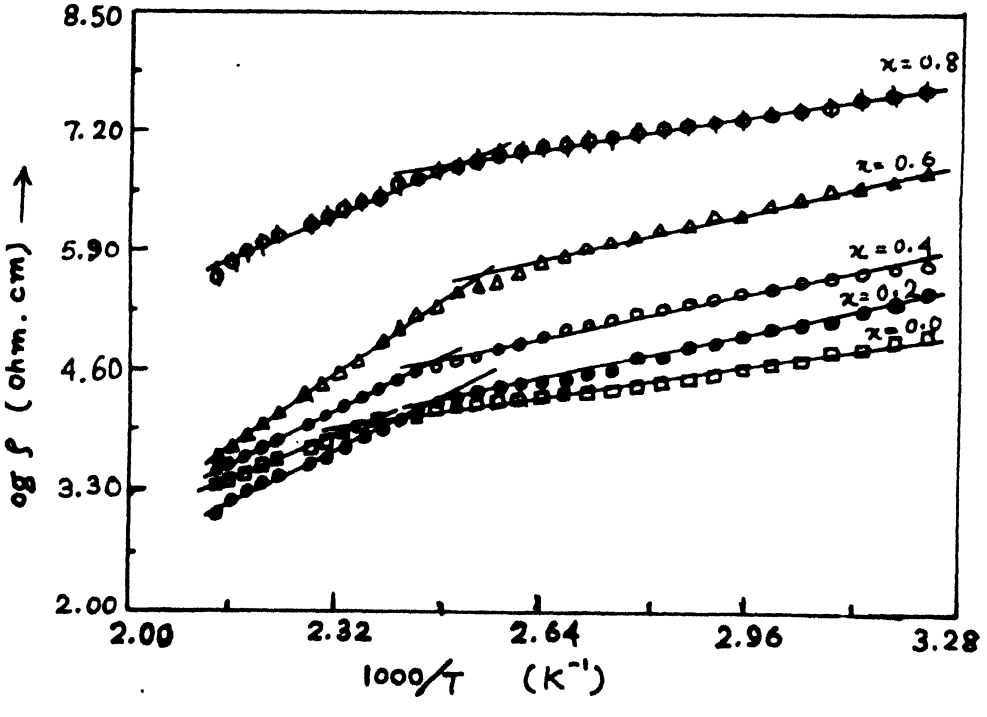

Figure 4. Variation of resistivity (log ρ) with temperature.

A-site [12] while the Sb^{5+} ions have preference for B-site [13,14]. Hence, cation distribution is assumed as above. From eq. (1), increase in Cr^{3+} content leads to a replacement of Fe^{3+} ions at B-sites. This relatively decreases the BB hopping between Fe^{2+} and Fe^{3+} ions, resulting in an increase in resistivity. The chromium ions do not participate in the conduction process but limit the degree of Fe^{2+}–Fe^{3+} transfer, thereby giving obstruction to the electron hopping [15], and increasing the resistivity. The temperature dependence of dc resistivity (log ρ) for all the samples in the range from 298 K to 473 K as shown in Figure 4 indicates that the electrical resistivity decreases as temperature increases. This may be due to the decrease in mobility of charge carriers and not due to the carrier concentration [9,16]. The temperature dependence in ferrites is governed by the relation

$$\rho = \rho_0 \exp(E_\rho/kT), \tag{2}$$

where ρ is the resistivity at an absolute temperature T, k is the Boltzman constant and E_ρ is the activation energy. However, the curves of log ρ *vs* $1/T$ is not linear and a change in slope is observed for all the samples studied. This change in slope was first anticipated to be due to the Curie temperature. But the observed Curie temperature does not correspond to the temperature at which the change in slope occurs. Similiar observations have been reported by other workers [2–4, 16]. The change in the slope of the curves of Figure 4 indicates the existence of two parallel conduction mechanisms with different activation energies [7]. Using relation (2) the activation energies were calculated for the two regions of different slopes with values ranging from 0.17 to 0.3 eV in the low temperature region

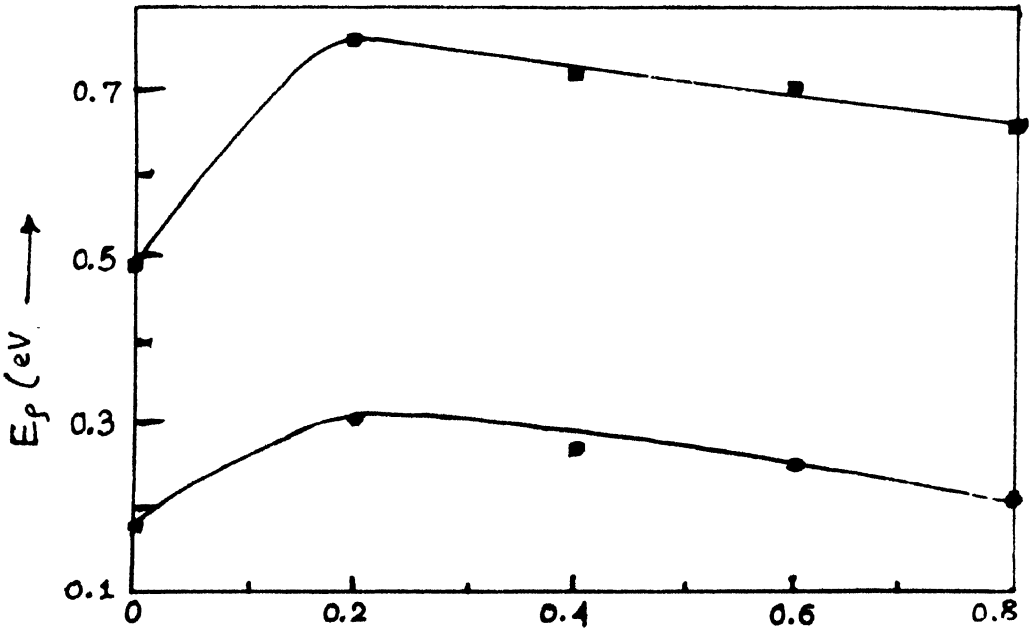

Figure 5. Activation energy as a function of chromium concentration.

(region I) and between 0.49 to 0.76 eV in the high temperature region (region II). Figure 5 shows the variation of activation energy as a function of Cr^{3+} substitutions. In region I, the conduction is attributed to the electron hopping between Fe^{+} and Fe^{3+} in the octahedral sites, as evident from the low activation energy. In region II, the high value of activation energy indicates that the conduction may be due to lithium ion conduction process (caused by lithium ions) [4, 16–18].

The variation of resistivity as a function of applied field (Figure 6) can be explained by considering the Heywang model [19] which suggests that besides the grain resistivity,

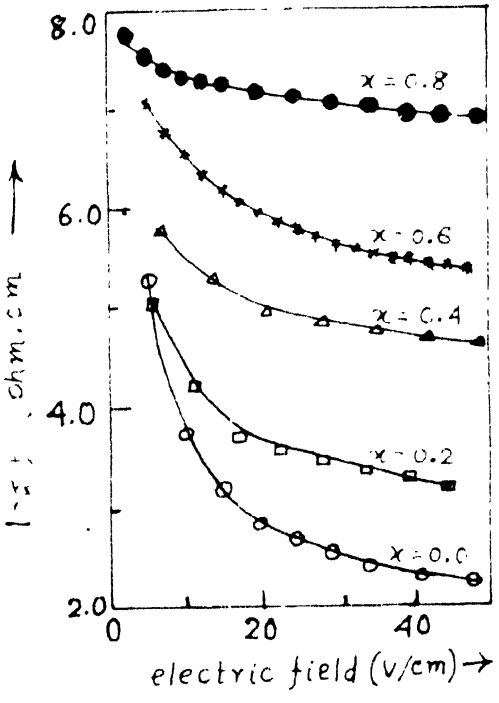

Figure 6. DC resistivity variation with applied dc electric field.

the grain boundaries also offer electrical resistance. According to Koops [20], the ferrite is assumed to consist of well conducting grains separated by poorly conducting layers known as the grain boundaries. These grain boundaries play an important role in determining the electrical properties of materials [21]. Due to structural and chemical disorders at the grain surfaces, there exists localised states in the forbidden gap. These states may trap electrons, resulting in a space charge region, which generates potential barriers on either side of the boundary. When an electric field is applied, the potential barrier and charge distribution is modified due to the change in the electron and hole concentration at the boundary resulting in an easy flow of charge carriers [15,22]; hence, the decrease in the resistivity with applied field.

The above discussion is supported by a study of the current voltage characteristics where each curve has two regions, an ohmic region and a non-ohmic one given by the

relation $I \propto V^{\alpha}$. The value of α in the non-ohmic region lies in between 2 and 3 for all the samples suggesting space charge limited conduction in inhomogeneous solids which contain grain boundaries [23,24].

Acknowledgments

The authors wish to thank the Department of Science and Technology, Govt. of India for the financial assistance. The authors also wish to thank the referee for helpful suggestions.

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